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PROCESS AND EFFLUENT CONTROL OF FLUORINE
AND FLUORIDE GASES IN THE CONVERSION OF
URANIUM ORES TO URANIUM HEXAFLUORIDE BY
GAS CHROMATOGRAPHY,

KENNETH W. CARPENTER

PREPARED FOR ORAL PRESENTATION
AT THE CANADIAN CHROMATOGRAPHY
CONFERENCE IN MONTREAL, CANADA.
APRIL 27-28, 1978

UNION
CARBIDE

PADUCAH GASEOUS DIFFUSION PLANT
PADUCAH, KENTUCKY

prepared for the U.S. DEPARTMENT OF ENERGY under
U.S. GOVERNMENT Contract W-7405 eng 26

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PROCESS AND EFFLUENT CONTROL OF FLUORINE AND FLUORIDE GASES
IN THE
CONVERSION OF URANIUM ORES TO URANIUM HEXAFLUORIDE BY GAS CHROMATOGRAPHY

Kenneth W. Carpenter

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NUCLEAR DIVISION

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Paducah, Kentucky

Prepared for the Department of Energy under
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Abstract

Process and Effluent Control of F_2 and Fluoride Gases in the Conversion of Uranium Ores to Uranium Hexafluoride by Gas Chromatography, Carpenter, K. W., Union Carbide Corp., Nuclear Division, Paducah, Ky. A brief description of the process and equipment involved in the conversion of UO_3 to UF_6 at the Paducah Gaseous Diffusion Feed Plant is given. This plant is a part of the uranium isotope enrichment complex operated by the Union Carbide Corp., Nuclear Division for the U.S. Department of Energy. The applications of specially designed corrosive gas chromatographs in analyzing and controlling critical stages in the process are described. Information is presented on the design and construction of the chromatographs. Special features include unique methods of simultaneously determining PPM concentrations of UF_6 and % levels of F_2 and air components in a minimum time, and determining O_2 , N_2 , F_2 , and HF concentrations in a single analysis. A description of specially coated teflon columns, selective sample component converters, and selective trapping systems used to resolve very difficult problems usually associated with the analyses of corrosive gases such as F_2 , HF, and UF_6 is presented.

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SUMMARY

The development of chromatographic instrumentation for the analyses of corrosive (halogenated) gases has evolved over a period of twenty or more years in the Union Carbide Corporation. Many of the techniques developed in the laboratories have been successfully implemented in field applications. By using the chromatographs, time consuming wet chemical analyses have been eliminated. Adapting the chromatographs to field service has made the analytical results immediately available to the process operators. Thus process control and efficiency has been improved and fluoride emissions to the environment have been reduced.

INTRODUCTION

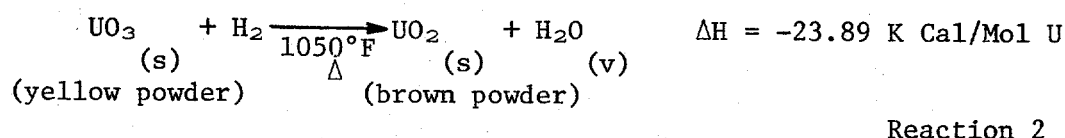
The Paducah Gaseous Diffusion Plant (PGDP) is operated by the Union Carbide Corporation, Nuclear Division (UCC-ND) under government contract for the U. S. Department of Energy (US-DOE). The purpose of the plant complex is to enrich the isotopic concentration of ^{235}U found in uranium ores and reprocessed uranium materials. The ^{235}U is enriched from a level of approximately normal (0.7% ^{235}U) to slightly enriched material (2 - 3% ^{235}U). The slightly enriched material is subsequently used at other facilities to prepare fuel elements for nuclear power reactors.

In the process of deriving isotopically enriched uranium from normal uranium, many chemical and physical processes are involved. Great demands are placed on analytical instruments to provide proper control over these processes. This paper briefly describes one step in uranium's long journey from the earth to electrical service for man and some of the analytical devices used in directing the course of the journey are discussed.

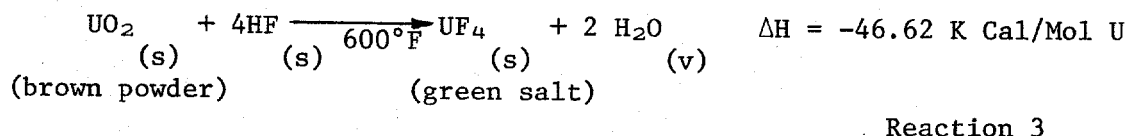
Feed uranium materials which are to be enriched must first be converted to the gas uranium hexafluoride (UF_6) before it is introduced into the enrichment cascade. At the Paducah Feed Plant, this conversion is accomplished in several discrete stages (Figure 1, Figure 2, and Slide 1). First ammonia (NH_3) is cracked to provide a source of hydrogen (H_2).



In the second step, uranium trioxide (UO_3) is reduced to uranium dioxide (UO_2) in fluid bed reactors using the cracked ammonia.

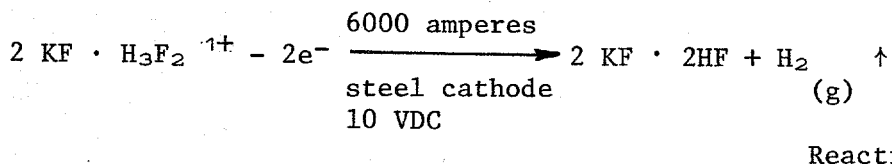
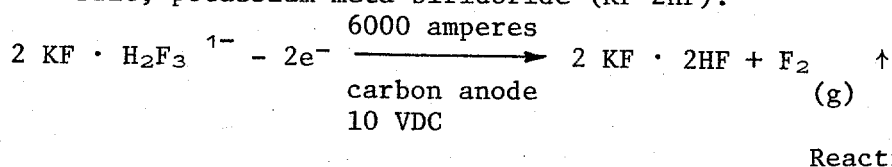


In the third step, the water vapor is vented and the solid uranium dioxide is hydrofluorinated to uranium tetrafluoride (UF_4) in ribbon-screw reactors.



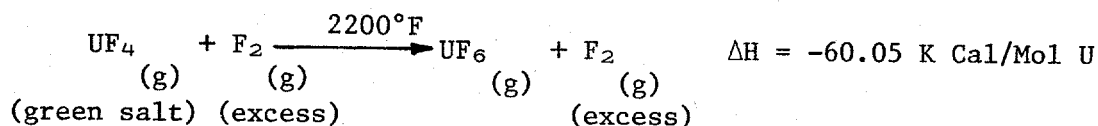
As UF_4 is formed, it can immediately be transferred for further processing to UF_6 or it can be stored and held for processing at a later date.

In the fourth step, elemental fluorine (F_2) is produced by the electrolysis of a molten salt, potassium meta-bifluoride ($\text{KF} \cdot 2\text{HF}$).



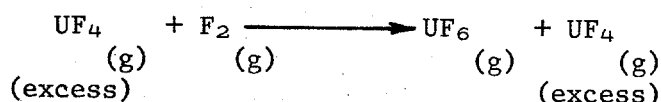
The cells operate at 180 - 200° F and the product is fluorine containing 6 - 8 mole % HF, 1 mole % air, and < 0.1 mole % CF_4 . Prior to transfer to the UF_4 - UF_6 reactors, the HF is recovered from the fluorine by cold trapping at -90° F. The fluorine reaching the reactors typically contains 96 mole % F_2 , 3 mole % HF, 1 mole % air, and < 0.1 mole % CF_4 .

The final stage in the conversion of uranium oxides to uranium hexafluoride occurs in the fluorination flame tower reactors. Here the green salt, uranium tetrafluoride (UF_4) is reacted with elemental fluorine (F_2) to form uranium hexafluoride (UF_6) (Figure 3, Slide 2).



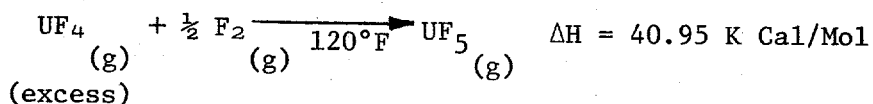
Reaction 6

An excess of F_2 is fed to the reaction so that the product gas is UF_6 containing 10 mole % F_2 . The UF_6 is stripped from the gas stream in an ammonia/glycol sublimation cold trap ($10\text{--}20^\circ\text{F}$). The off-gas from this system passes to a clean-up reactor (CUR) which reacts the residual fluorine with an excess of solid uranium tetrafluoride to form uranium hexafluoride.

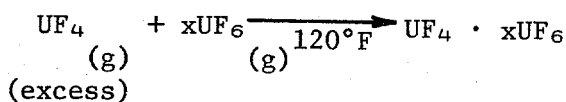


Reaction 7

Final extraction of the uranium hexafluoride from the process gas stream is made in an ammonia/carbon dioxide sublimation cold trap (-40°F). The off-gas from this system contains less than 2 mole % F_2 and less than 0.05 mole % UF_6 . This gas stream then passes through a fluid bed absorber (FBA) which strips the residual F_2 and UF_6 from the gas stream before venting to the atmosphere.



Reaction 8



Reaction 9

The UF_6 is typically less than 50 PPM molar and the F_2 is less than 1 mole % in the vent gas from the fluorination system.

The analytical instrumentation described in this paper is used to monitor and control the fluorination process and fluoride emissions from the fluorination system. Monitoring and control is conducted at four points in the process (Figure 3, Slide 2).

(1) The fluorine fed to the fluorination tower reactors is monitored using a gas chromatograph. This instrument analyzes and records the concentrations of F_2 , O_2 , N_2 , CF_4 , and HF . The F_2 concentration determines the operating conditions necessary for efficient fluorination reactions. Tower reaction rate control is accomplished by varying feed rates of UF_4 and F_2 . This monitoring station allows system inleakage or significant process failure in the fluorine plant to be detected at an early stage.

(2) The concentration of excess fluorine in the product UF_6 (fluorination tower reactor outlet) is carefully monitored by an UV photometric analyzer. At this point, the excess F_2 must not be less than 4 mole % or the fluorination reaction will be compromised and the towers will plug. The excess F_2 must not be greater than 10 mole % or the fluid bed absorber will pass fluorides to the environment. The photometric analyzer provides real time analyses of the fluorination reaction and very efficient control is maintained in this stage of the process.

(3) The third monitoring and control point is located immediately downstream of the FBA. A gas chromatograph monitors the vent gas from the FBA for concentrations of F_2 and UF_6 .

(4) The fourth and final monitoring and control point is the "Total Vent Flow Control Station". Monitoring the vent flow is a differential pressure transmitter reading the pressure drop across a calibrated flow orifice. A continuous read-out of the vent flow and pressure is recorded on a strip chart recorder in the central control room. Vent flow and chromatographic records provide an accurate and continuous record of the amounts of fluorides and uranium materials emitted to the environment from the feed plant.

The chromatographs used in feed plant service are basically modeled after those developed by C. W. Weber, et. al., ORGDP, Oak Ridge, Tennessee, and Rosmassler, Mayo, and Harris,⁽¹⁾ PGDP, Paducah, Kentucky. The basic units have been modified to suit the specific needs in the feed plant.

The first chromatograph in the system (control point no. 1) samples the F_2 header supplying F_2 to the fluorination tower reactors. This chromatographic system uses a split column arrangement with a single gas density detector, (Figure 4, Slide 3). The sample loop and injection system is formed using two Whitey Multi-Port Ball Valves (Model 43Y Series), interconnecting tubing, and a Whitey 90° Spring Return Air Operator (Model MS-133SR). All wettable portions of the sampling system are either teflon, nickel or monel. Sampling and analyses are automatic using an ATC timer-programmer. Argon is used as the carrier and reference gases because we desire to measure O_2 and N_2 in the process fluorine. Immediately after the sample is swept from the loop, the carrier gas stream splits with one-tenth the total flow directed through a capillary restrictor passing to a NaBr converter and then into a 1/4" O.D. x 20' teflon column. The F_2 in the sample is converted to Br_2 in the NaBr converter. The teflon column then separates the components of air, Br_2 , HF, CF_4 , etc.

The conversion of F_2 to Br_2 is necessitated by the fact that O_2 and F_2 are not resolved (separated) by the teflon columns used for corrosive gas chromatography. In a sample containing both O_2 and F_2 , the two compounds would elute from the column simultaneously and the analyses for either would be biased by the presence of the other. Converting the F_2 to Br_2 before the sample reaches the column allows the O_2 to be separated from the Br_2 . An indirect measurement for F_2 concentration is thus made. Either NaBr or NaCl can be used successfully. NaBr is preferred due to the increased sensitivity of Br_2 over Cl_2 when using a gas density detector.

The balance (nine-tenths) of the carrier flow is directed into a NaF trap and charcoal converter. The NaF trap strips the HF from the sample and the charcoal converts the F_2 to CF_4 . Thus neither HF or F_2 is allowed to pass to the mole sieves column which would be destroyed by either of these materials. The sample sweeps from the converter into a 1/4" O.D. x 6' 5A mole sieves column which resolves the components of O_2 and N_2 . At 120°F the CF_4 is permanently absorbed on the charcoal or mole sieves. After elution from the columns, the two carrier gas streams recombine before entering the Gow-Mac gas density detector (Figure 4, Slide 6). The argon carrier gas stream, sweeping the sample components into the detector sequentially, is compared electronically with the reference side of the gas density detector. The sensing elements of the detector are formed by a matched pair of ohmic thermistors rated at 9,000 ohms each. The design of the gas density detector is such that the thermistors are never exposed to the corrosive halogenated sample. Each thermistor element is incorporated in opposing branches of a wheatstone bridge circuit. The detector senses any difference in the densities of the reference and carrier gas streams as an imbalance in the wheatstone bridge circuitry. This imbalance is amplified and recorded as shown on Figure 5, Slide 4. A sample chromatogram is shown in Figure 6, Slide 5. The effluent from the chromatographic system is cleaned of fluorides in a solid sorbent chemical trap before being vented to the atmosphere.

The second monitoring and control point in the system (control point no. 2) utilizes a Teledyne UV Photometric Analyzer, Series 600 to analyze the concentration of excess F_2 at the outlet of the fluorination tower reactors. This is an unique application of a UV analyzer in that spectral absorbance in the measuring region (347 nm) due to UF_6 is electronically subtracted by reference to a region of absorbance specifically due to UF_6 (407 nm). As F_2 absorbs at the 347 nm region but not at the 407 nm region, the instrument can thus sense F_2 in the presence of varying concentrations of UF_6 (Figure 7, Figure 8, and Slide 6). Information from this analyzer is also used to control the feed rates of reactants to the fluorination tower reactors.

The second chromatograph in the system samples the outlet of the FBA (control point no. 3). Information from this instrument is used to adjust the feed rates of UF_4 to both the CUR and the FBA. A single line diagram of the chromatographic system is shown in Figure 9, Slide 7. An air carrier gas is used to sweep a measured volume of sample gas from the sample loop into the system of NaF-NaBr trap and converter and into the chromatograph columns.

The columns used are made by coating 40-60 mesh teflon, Johns Mansville 6H Molding Powder, with a halocarbon oil (Hooker Chemical Co., Type FS-5). The oil is applied by dispersion in Freon-113 solvent with subsequent vacuum distillation and drying of the oil coated particles. The ratio of oil to powder is 16% w/w. The oil coated powder is chilled with dry ice and then gently packed into a 1/4" O.D. teflon tube. Prior to service the new column is passivated by purging with 1% fluorine in nitrogen at 10 sccm for 12 hours. The temperature is held at 120° F during the passivation treatment.

The sample loop is formed by a multi-port teflon plug valve and interconnecting tubing. All wettable portions of the sample handling system are either teflon, nickel, or monel. Immediately after the sample loop, the carrier gas stream is split by using a nickel capillary restrictor (0.017" I.D. x 30" l) and

teflon column (1/4" O.D. x 2' 1) in one leg, and the natural restriction of the NaF-NaBr trap/converter (1/4" O.D. x 18" 1) and teflon column (1/4" O.D. x 30" 1) in the other leg. The capillary effects a 75/25 split of the carrier gas stream, 75% passing to the short column and 25% passing to the long column. As the gas streams elute from each column, they recombine before entering the gas density detector. The effluent from the system is stripped of fluorides in a solid sorbant chemical trap before venting to the atmosphere.

In order to measure UF_6 at the 20 PPM level, the major portion of the sample (75%) is routed to the short column where only the UF_6 is separated from the other components. All other components of this portion of the sample elute simultaneously and give rise to the peak identified as "composite" in the sample scans (Figure 10, Slide 8).

A dual amplifier recorder (Tracor Westronics, Model D11E; 0-5 and 0-10 mV ranges) is used to amplify and record the output from the detector. As shown in Figure 11, Slide 9, the 0-5 mV amplifier receives input from an attenuated voltage divider which allows one-half strength signal (x2 attenuation) to pass. Although this allows the signals from other components in the sample to overwhelm the 0-5 mV amplifier, it does recover in time to respond correctly to the signal from any UF_6 in the sample. UF_6 in the concentration range of 10-20 PPM is readily measured with this system.

The second amplifier (0-10 mV) receives signal through a second voltage divider attenuator which is set to a less sensitive setting (x20 attenuation) to measure the signals from HF, CF_4 , and F_2 at concentrations of 0-1 mole %. The analyses of HF, F_2 , CF_4 , and UF_6 in the presence of air is normally quite complex and time consuming. The teflon columns required for corrosive halogen gases will resolve the lighter components (Br_2 , O_2 , HF, CF_4 , etc.) in approximately 10 minutes using a 30' column. However, if the column is sufficiently long to resolve the light components, the elution time of UF_6 becomes inordinately long (1-2 hours). For meaningful process control, the monitoring system must provide a complete analyses of all fluorides including UF_6 in 10-15 minutes. By using the chromatographic system described, these objectives are obtained. Three typical chromatograph scans are shown in Figure 11, Slide 13.

Table 1 shows comparative data from both field chromatograph analyses and laboratory titration analyses. Both methods yield reasonably comparative results. It should be noted that the laboratory titrations were from intermittent samples throughout the month. The chromatographic data is from continuous sampling throughout the same time period.

Table 2 shows the relative retention times for various gases on the teflon columns used in this study.

These adaptations of the corrosive gas chromatographs in the feed plant have resulted in improved control and efficiency and have provided excellent monitoring, records, and improved control of fluoride emissions.

Table 1

FLUORINATION PLANT VENT STACK ANALYSES

Date	Field Chromatograph Analyses ^(a)			Laboratory Titration Analyses ^(b)		
	UF ₆ (PPM Molar)	F ₂ (% Molar)	HF (% Molar)	UF ₆ (PPM Molar)	F ₂ (% Molar)	HF (% Molar)
Oct. 1976	37	0.8	1.40			
Nov. 1976	35	0.7	1.60			
Dec. 1976	36	0.7	1.56			
Jan. 1977	50	4.0	1.50			
Feb. 1977	100	5.4		100	4.4	1.6
Mar. 1977	20	3.5		<100	3.9	
Apr. 1977 ^(c)	20	11.8		100	5.7	1.6
May 1977	20	7.1				
June 1977	23	7.8				
July 1977 ^(d)	250	3.3		300	4.2	
Aug. 1977				200	5.0	1.5
Sept. 1977	37	0.8	2.00	128	3.8	2.0

(a) Chromatographic data is average values from 875 analyses per month.

(b) Laboratory titration data is average values from 79 analyses per month.

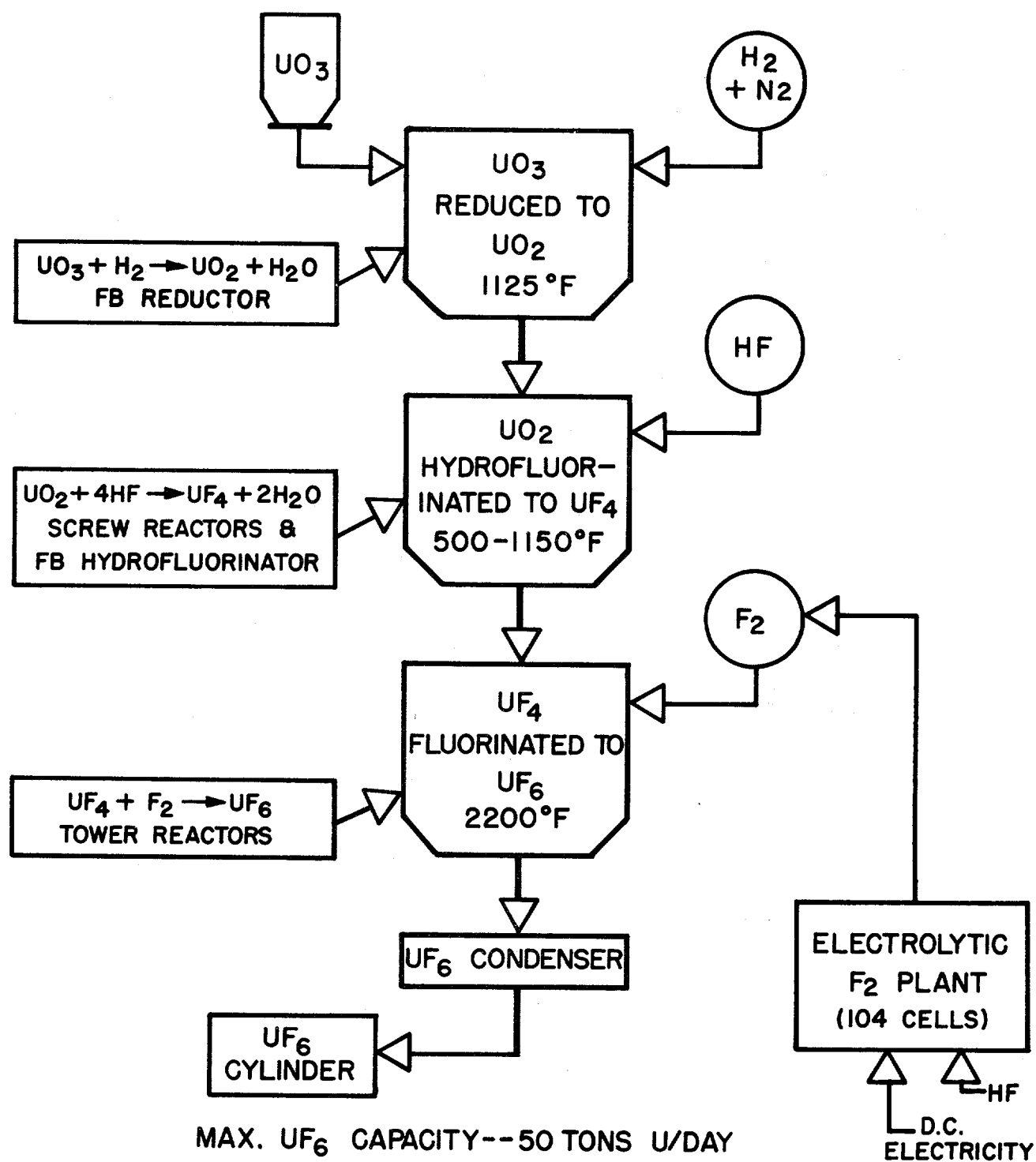
(c) Began to process low assay and scrap materials in shut-down operations.

(d) Fluid bed absorber was not in operation during July, 1977.

Table 2

PERFORMANCE DATA FOR TEFLON COLUMN^(a)

<u>Gas</u>	<u>Retention Time (Sec.)</u>	<u>Sensitivity (mV/μMole)</u>
O ₂	320	
F ₂	320	0.3910
HF	400	
Cl ₂	500	0.4204
UF ₆	3960 (Long column)	
	420 (Short column)	4.8872



PADUCAH FEED PLANT

Fig. 1

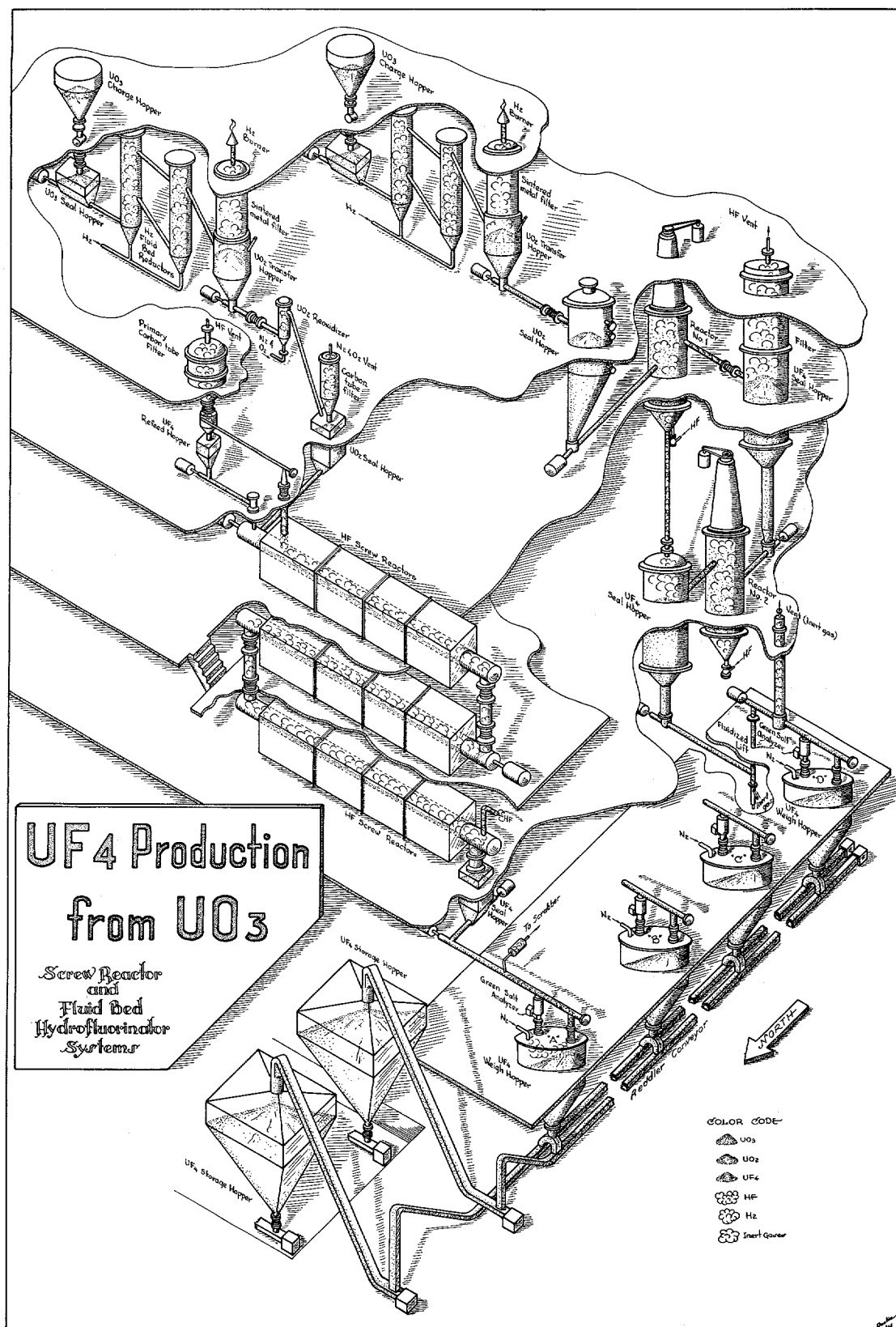


Figure 2

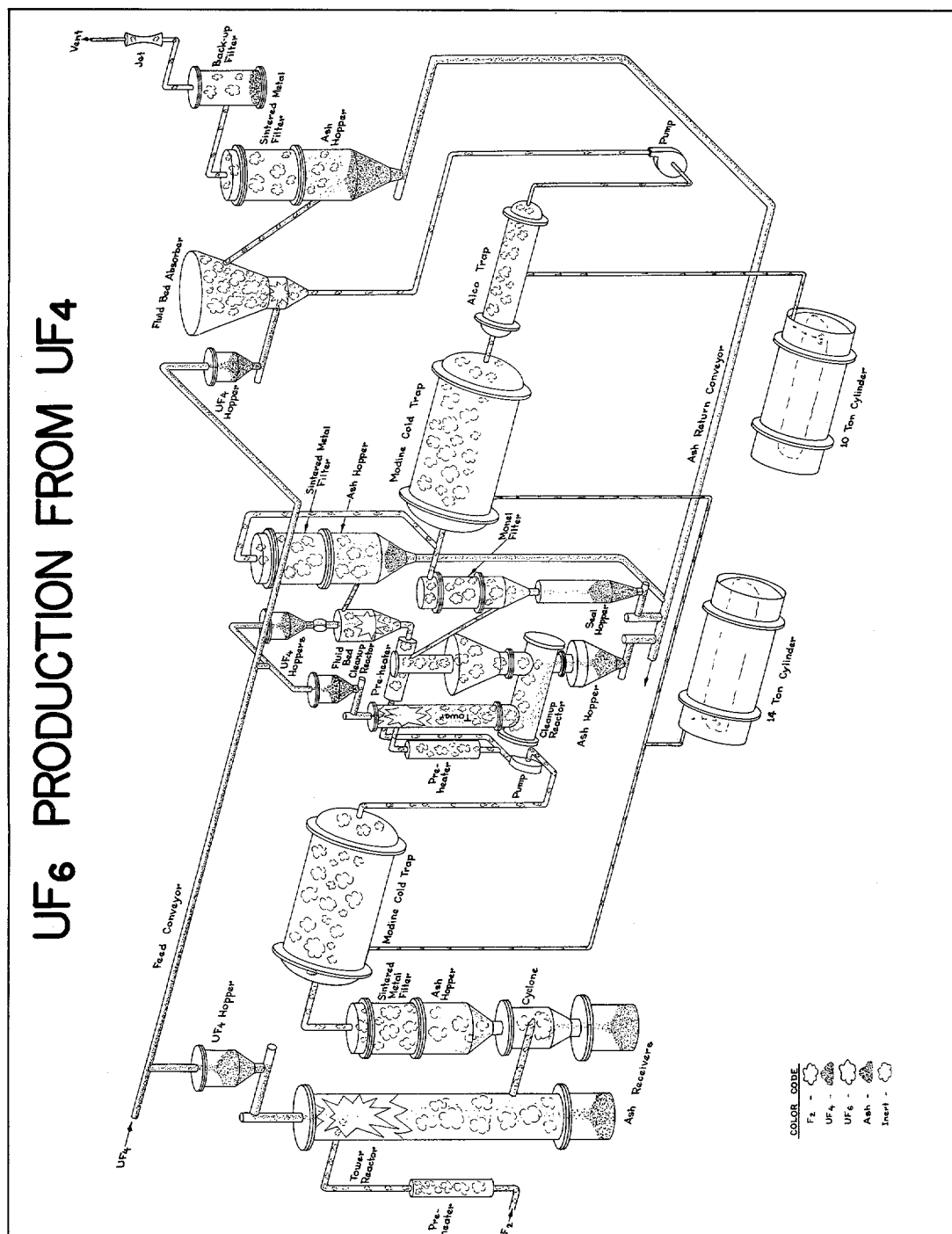
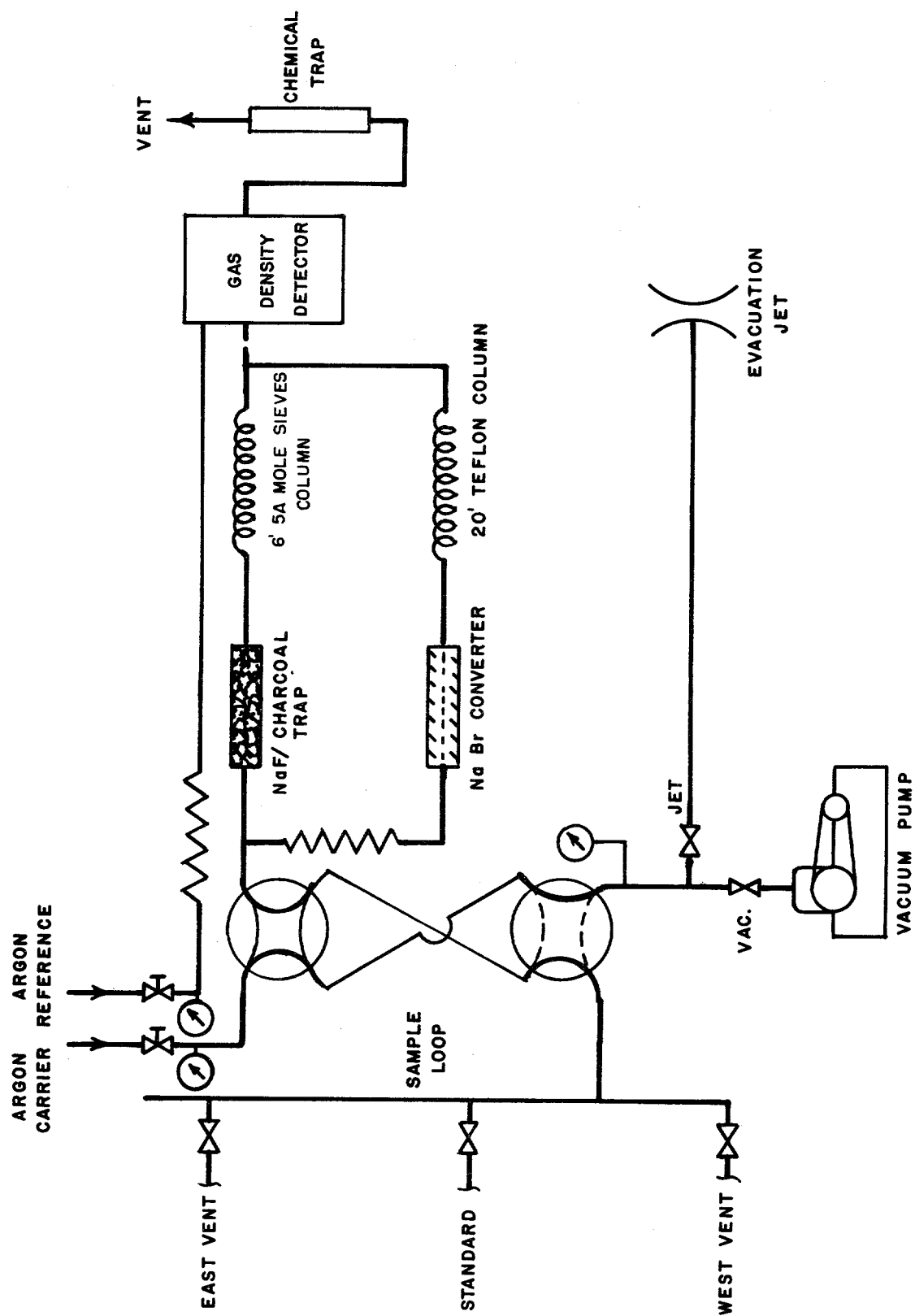
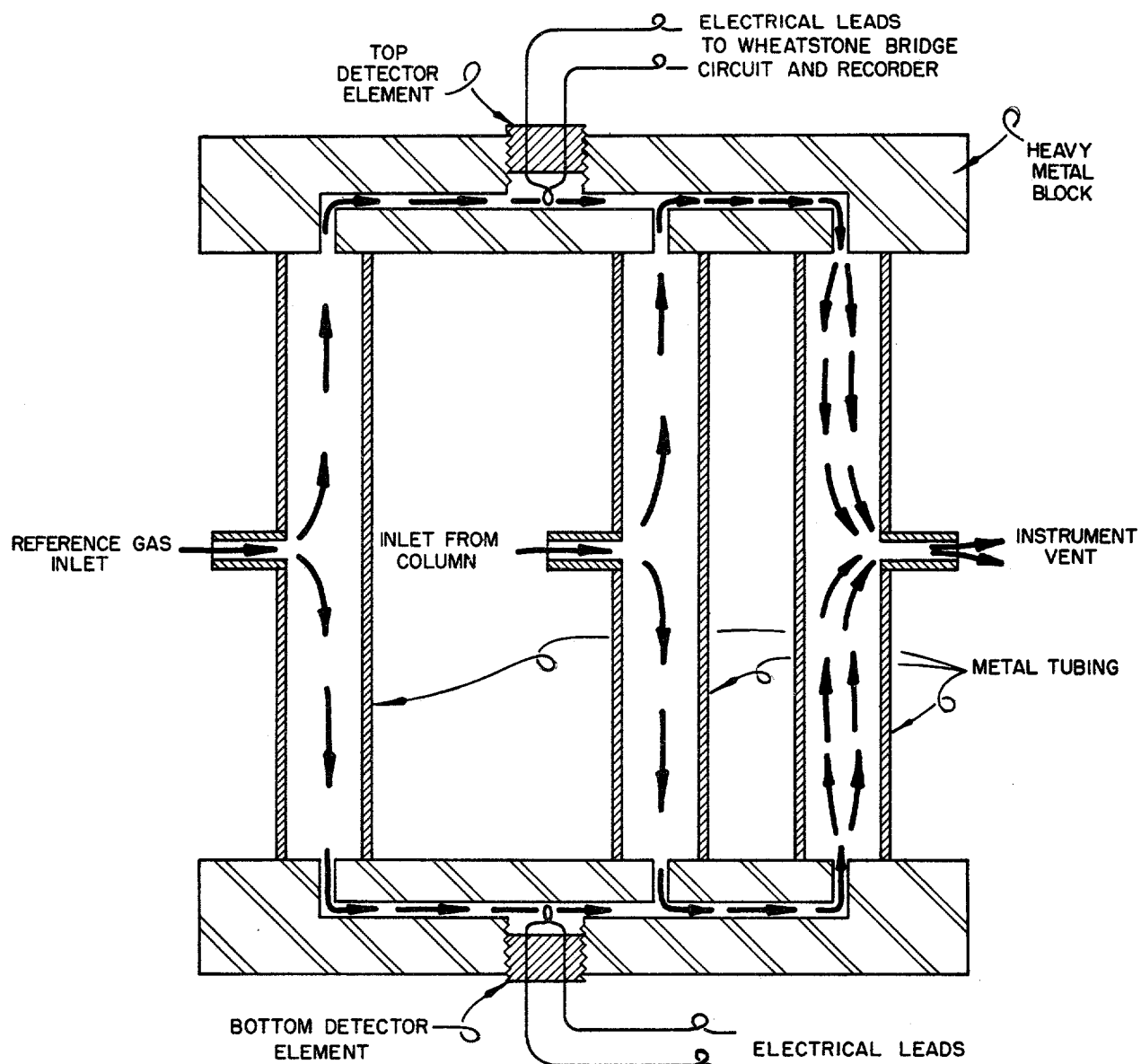


Figure 3



CORROSIVE GAS CHROMATOGRAPH FLOW SCHEME

Fig. 4



GAS DENSITY DETECTOR

Fig. 5

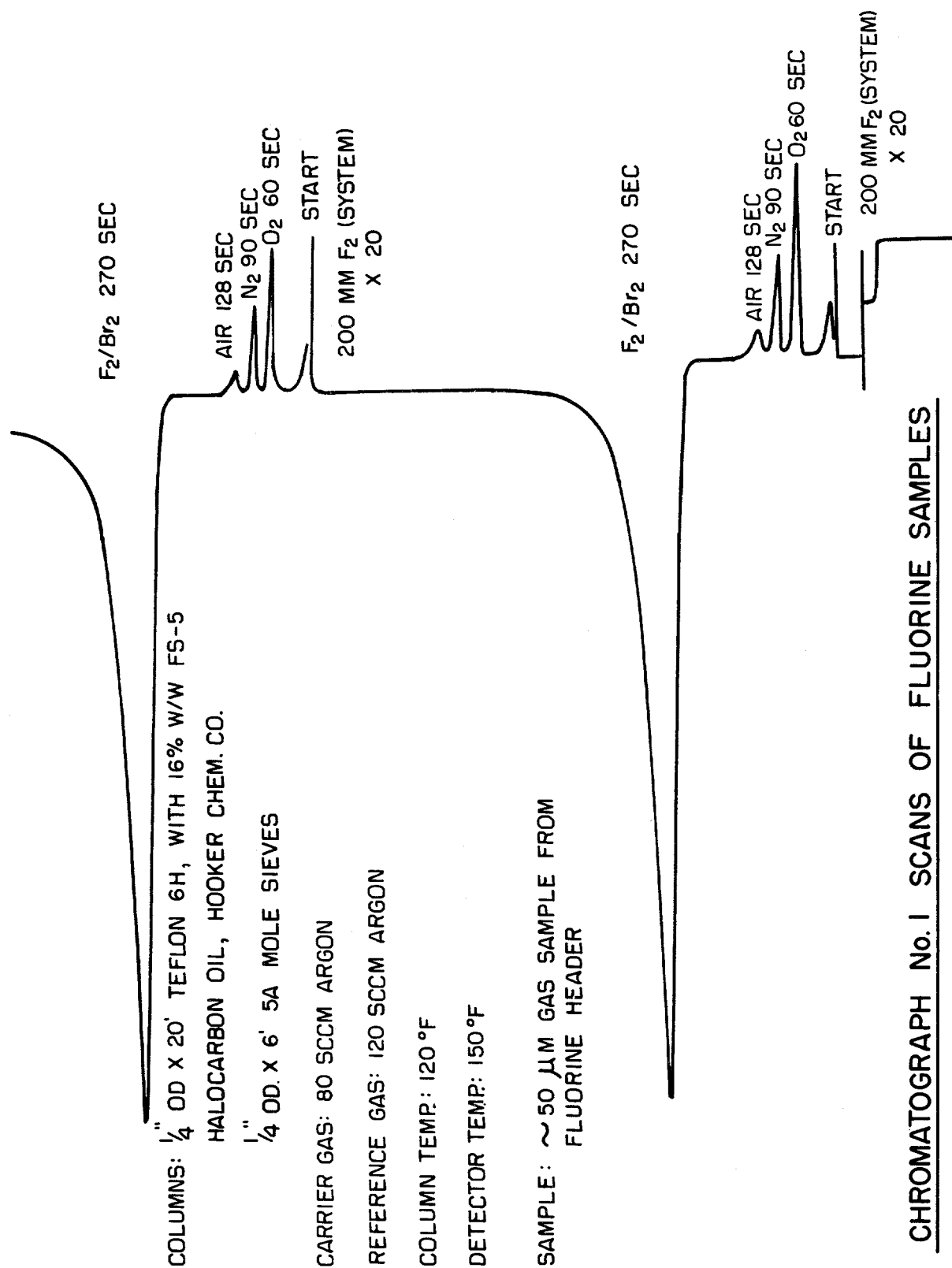
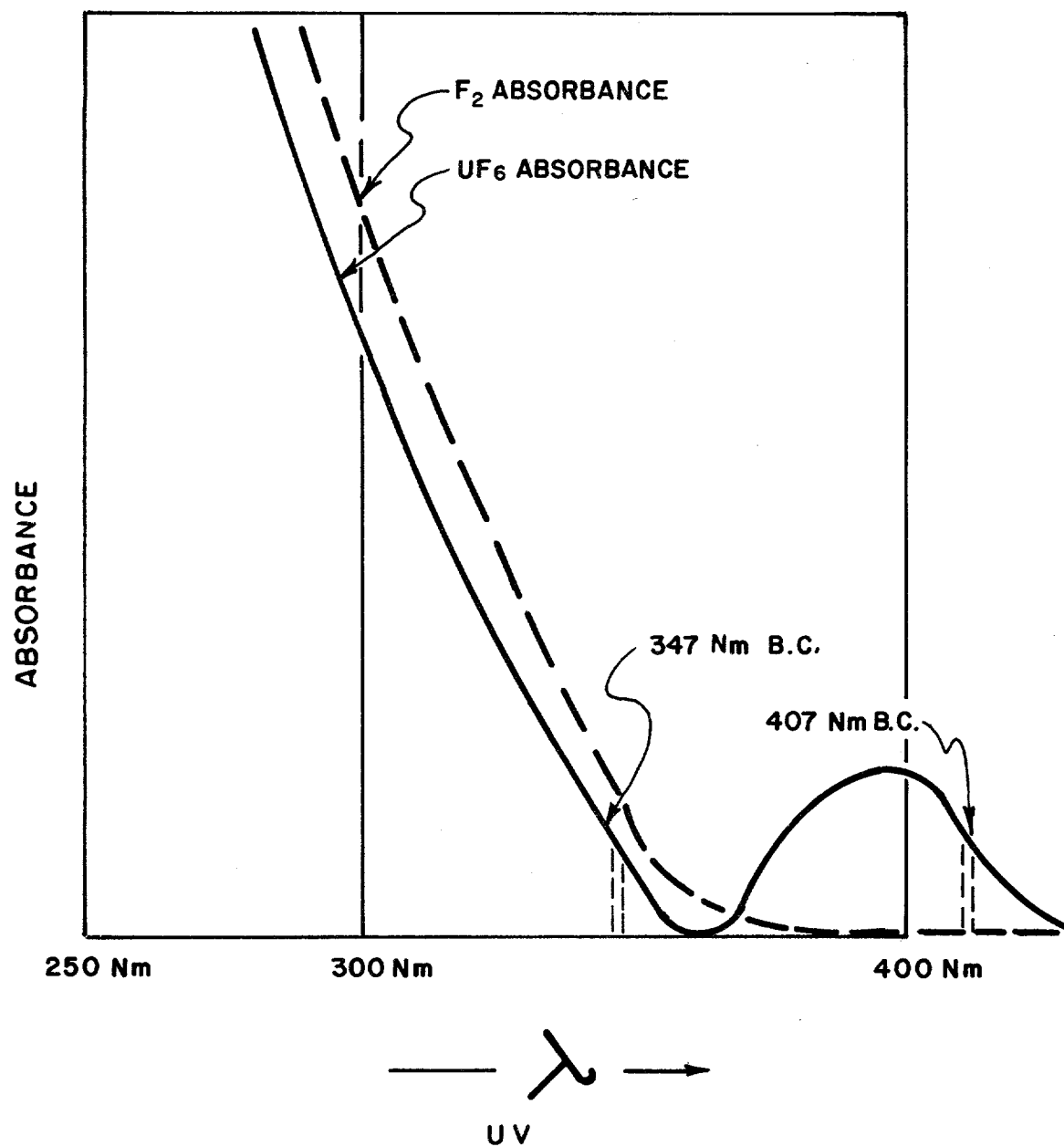


Fig. 6



LEGEND

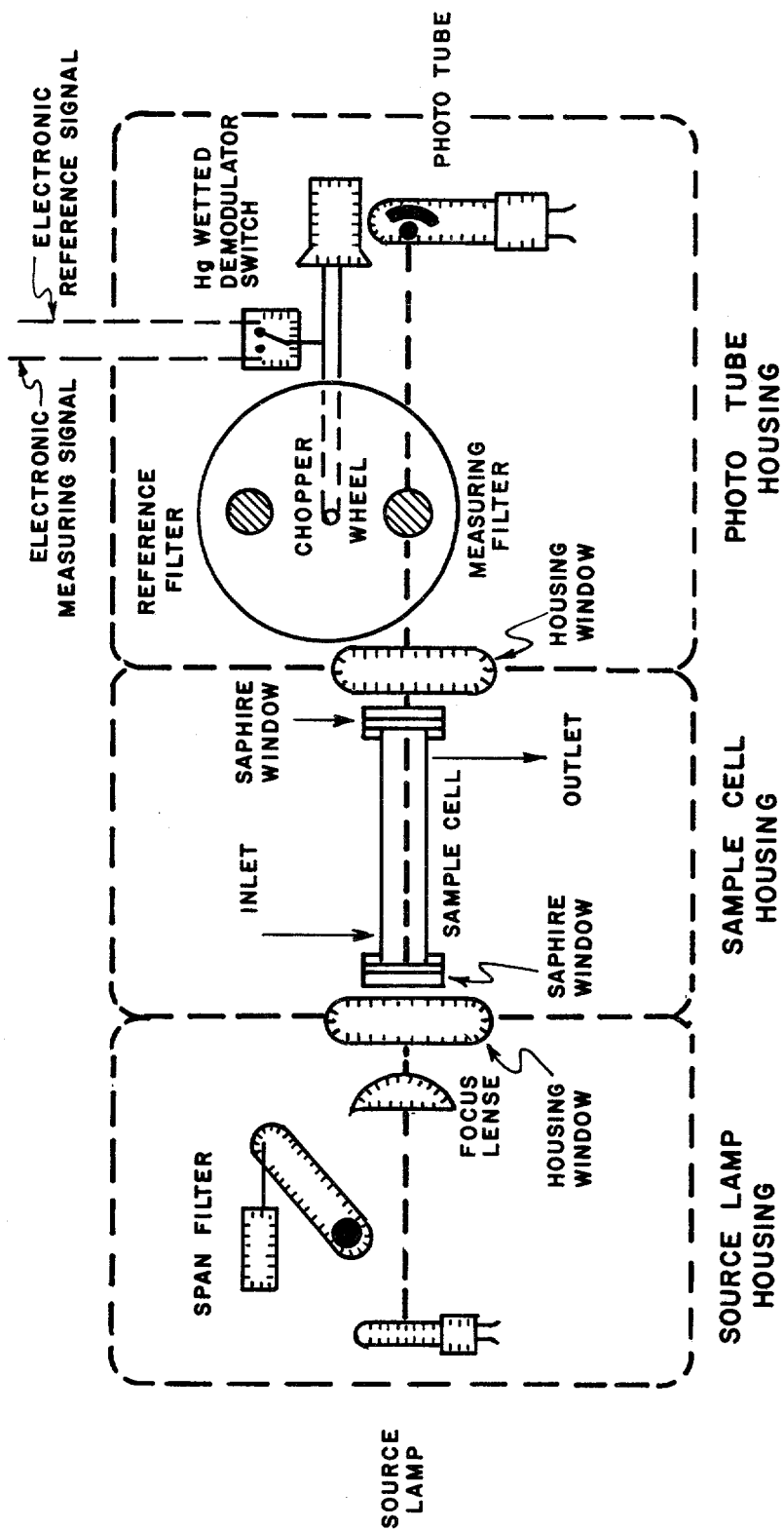
B.C. = BEAN CENTER

--- F_2 ABSORBANCE

— UF_6 ABSORBANCE

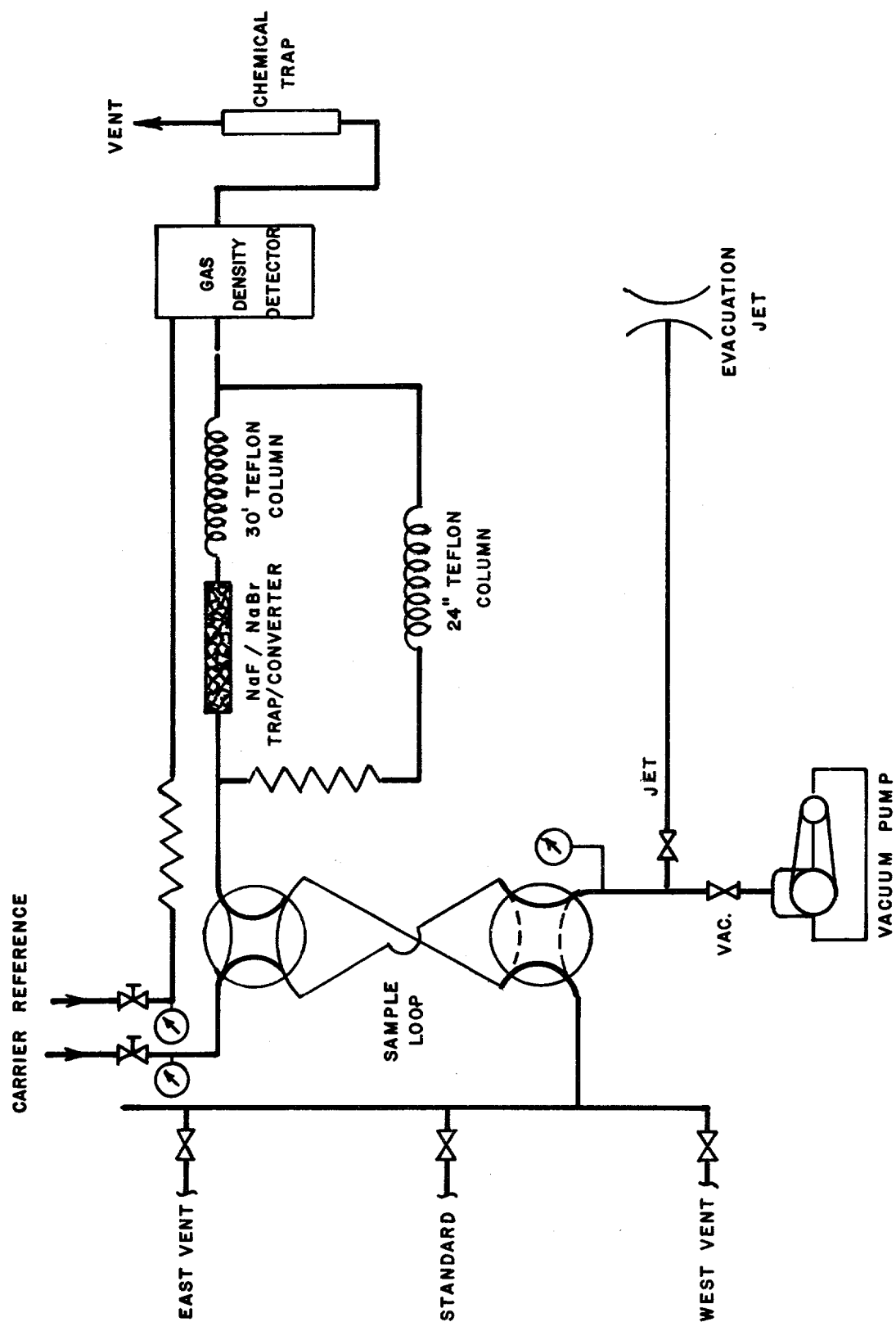
UF_6 & F_2 SPECTRAL ABSORBANCE IN UV REGION

Fig. 7



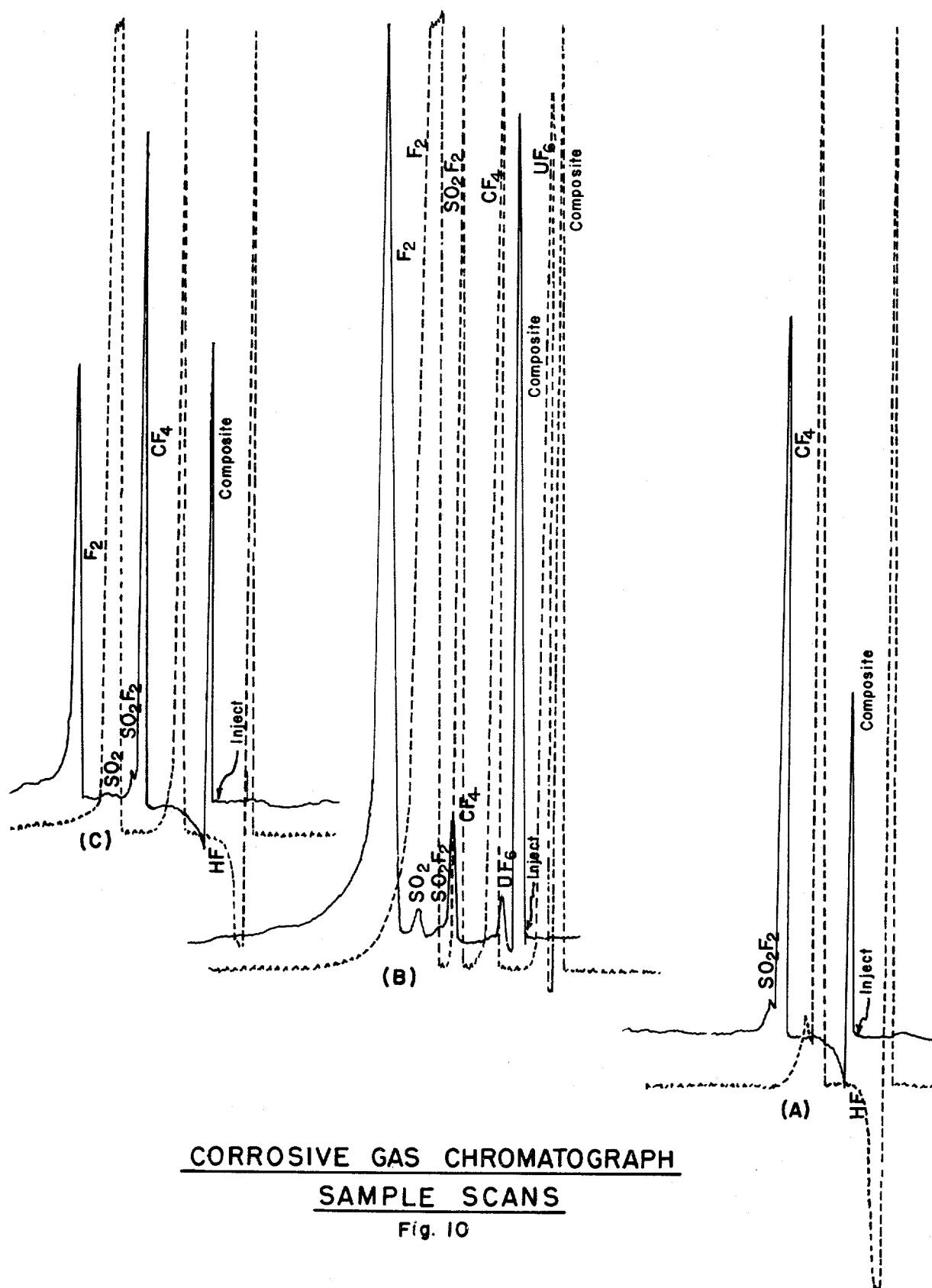
TELEDYNE F₂ ANALYZER COMPONENT SYSTEM

Fig. 8



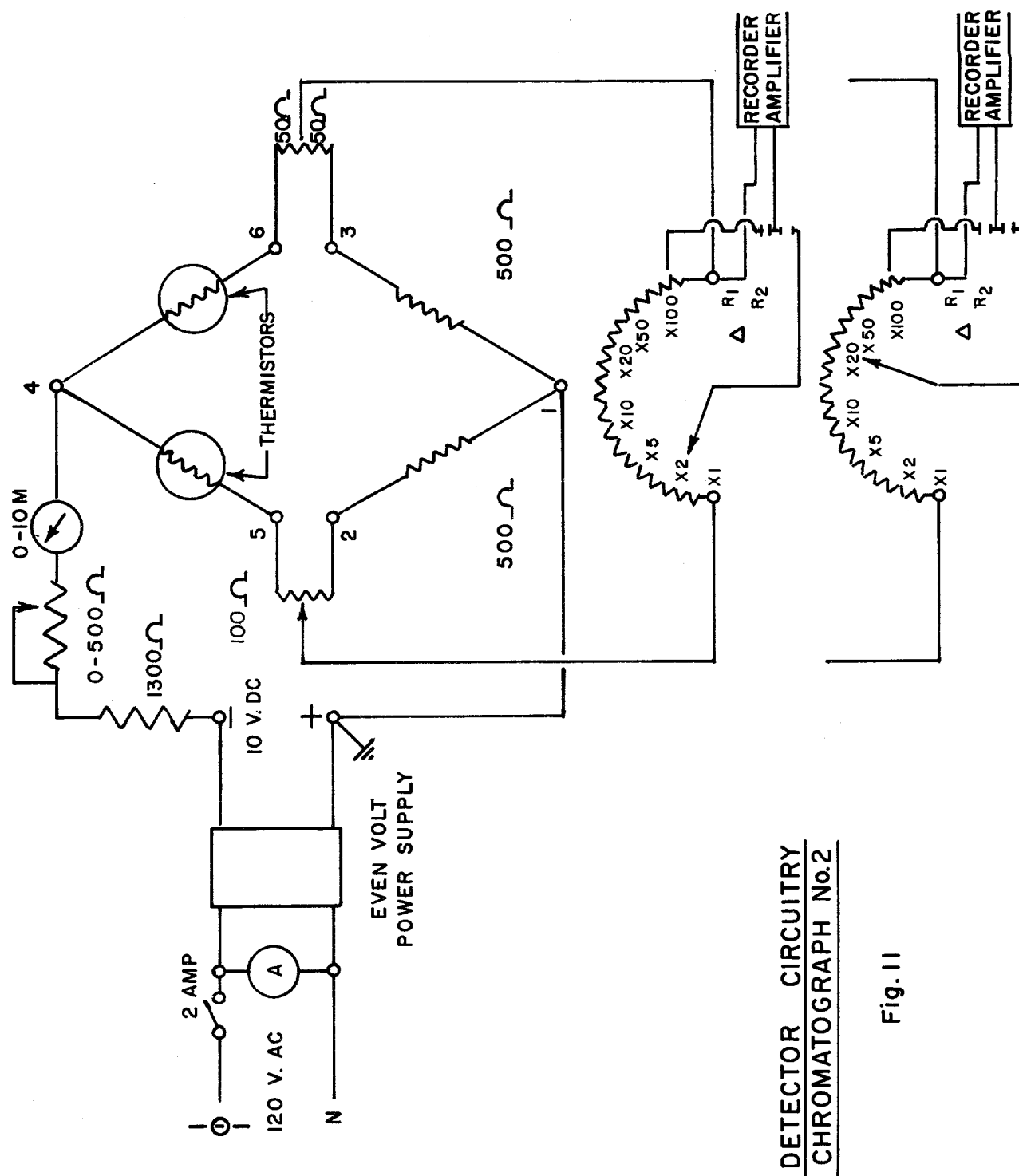
CORROSIVE GAS CHROMATOGRAPH FLOW SCHEME

Fig. 9



CORROSIVE GAS CHROMATOGRAPH
SAMPLE SCANS

Fig. 10



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